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Cascading One-Pot Synthesis of Single-Tailed and Asymmetric Multitailed Giant Surfactants

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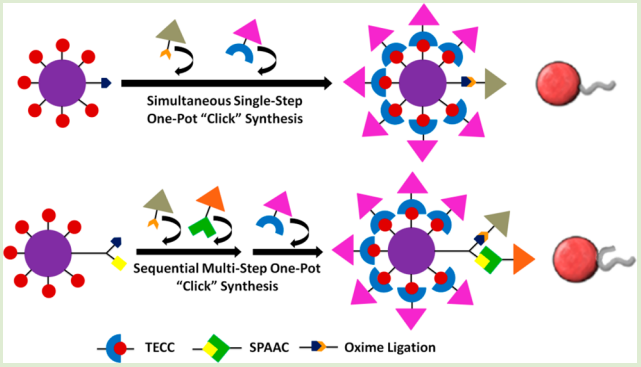
Supporting Information

ABSTRACT: Rapid and precise synthesis of macromolecules has been a grand challenge in polymer chemistry. In this letter, we describe a convenient, rapid, and robust strategy for a one-pot synthesis of various precisely defined giant surfactants based on polyhedral oligomeric silsesquioxane (POSS). The method combines orthogonal oxime ligation, strain-promoted azide−alkyne cycloaddition (SPAAC), and thiol−ene "click" coupling. The process is usually completed within 0.5−2 h and does not require chromatography methods for purification. With near quantitative conversion efficiency, the method yields giant surfactants with distinct topologies, including single-tailed and asymmetric, multitailed giant surfactants. Both polymer tail composition and POSS surface chemistry are controlled precisely and tuned independently, enabling the design and preparation of new classes of giant surfactants.



The bottom-up approach to macromolecular synthesis facilitates controllable and reliable fabrication of complex, multidimensional nanostructures with nearly atomic precision.[1−3] Using these principles, a large number of intriguing supramolecular structures with different shape, geometry, and function are now readily available.[4−6] The spontaneous self-organization of macromolecules offers many advantages in nanotechnology. In particular, directed self-assembly of giant surfactants plays an increasingly important role for constructing diverse structures with nanometer feature sizes.[7−12]

Giant surfactants are a subclass of giant molecules and describe polymer-tethered nanoparticles in general.[7,8,13] They capture the essential structural feature of small-molecule surfactants but possess a much larger size at several nanometers. Various giant surfactants with distinct architectures have been designed and synthesized similar to the spirit of size amplification of their small-molecule counterparts, such as giant lipids with symmetric/asymmetric tails,[14,15] giant gemini surfactants,[16,17] giant bolaform surfactants,[16] and multi-headed/multitailed giant surfactants.[16,18] Giant surfactants are attractive in several applications due to their versatile, self-assembled supramolecular structures with sub-10 nm feature sizes.[7,8] This class of unique materials bridges the gap between two classes of different-sized amphiphilic molecules (small-molecular surfactants and block copolymers). They possess features of both material classes in terms of their self-assembly behaviors in bulk and in solution.

Recently, extensive efforts have been devoted to developing polyhedral oligomeric silsesquioxane (POSS)-based giant surfactants with an emphasis on precision synthesis and structural variations.[8,16,18] The T_8 POSS is perhaps the smallest silicon nanoparticle with a cage diameter of around 1.0 nm. Due to its 3D-conformational rigidity and readily modifiable surface chemistry, it has been used widely as a building block for giant surfactants.[19−25] Moreover, it affords the precise control of size, symmetry, number, and location of functional groups on the surface, which is highly desired in the design of novel giant molecules.[26] Both "grafting-from" and "grafting-to" strategies have been used successfully for the design and synthesis of POSS-based giant surfactants with different architectures.[14,17,18,27,28] The success of a "grafting-from" approach relies on the compatibility of the vinyl POSS

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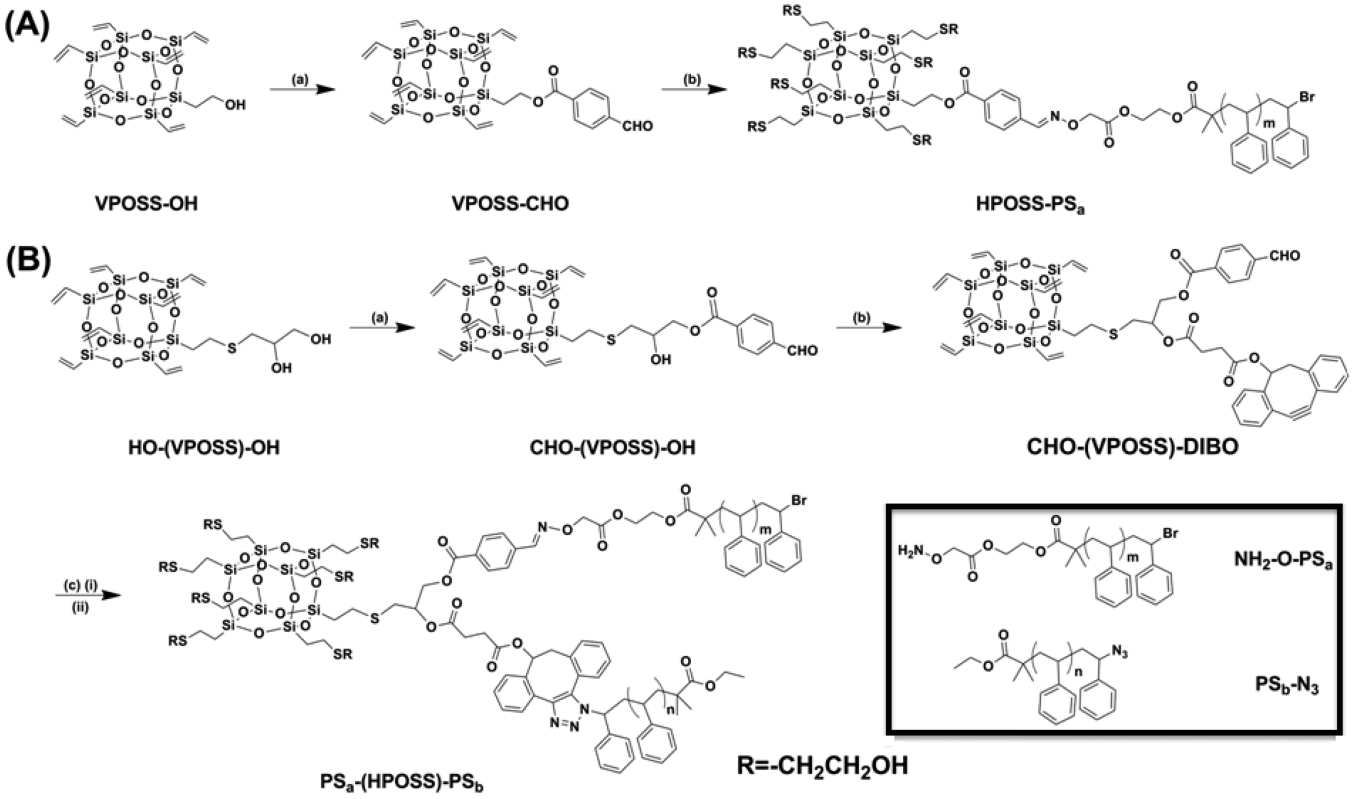
Scheme 1. One-Pot Synthetic Approaches for Two Types of POSS-Based Giant Surfactants[a]



[a](A): (a) 4-Formylbenzoic acid, DPTS, DIPC, dry CH_2Cl_2, 0 °C, 92%; (b) NH_2-O-PS_a, TsOH, 2-mercaptoethanol, DMPA, THF, 25 °C, UV, 30 min, 82%. (B): (a) 4-formylbenzoic acid, DPTS, DIPC, dry CH_2Cl_2, 0 °C, 53%; (b) DIBO−COOH, DPTS, DIPC, dry DMF, 0 °C, 90%; (c) (i) NH_2-O-PS_a, TsOH, PS_b-N_3, THF, 25 °C, 1.75 h, without further purification; (ii) 2-mercaptoethanol, DMPA, THF, 25 °C, UV, 15 min, 84%.

(VPOSS) cage to different polymerization conditions, such as ring-opening polymerization (ROP)[27] or atom transfer radical polymerization (ATRP).[14] However, these methods often suffer from inefficient initiations and lack good molecular mass and mass distribution control on the grafted polymer chains.[14] In contrast, a "grafting-to" strategy seems to be a more general, versatile, and precise way toward diverse giant surfactants with well-controlled molecular mass, chemical composition, molecular weight distribution, and macromolecular architectures.[17,18,28]

The emergence of "click" chemistry offers several modular, robust, and efficient chemistries that enable the "grafting-to" strategy to greatly simplify the construction of POSS-based giant surfactants.[17,29] Specifically, a sequential "click" approach consisting of Cu(I)-catalyzed [3 + 2] azide−alkyne cycloaddition (CuAAC) and thiol−ene "click" coupling (TECC) reactions[30−33] has been developed and facilitated the synthesis of a number of giant surfactants.[16,28] By taking advantage of strain-promoted azide−alkyne cycloaddition (SPAAC), a recent addition to the ever-expanding "click" toolbox,[34−37] our group has successfully developed a sequential triple "click" route toward multiheaded and multitailed giant surfactants based on the drastic difference in reactivity between SPAAC and CuAAC in the absence of Cu(I).[18]

The incorporation of new reactions into the established "click" toolbox not only broadens the scope of the sequential "click" chemistry approach but also allows the development of a one-pot synthetic procedure by using completely orthogonal "click" reactions in a single step or performing cascading multistep reactions in a sequential manner.[29,38] A one-pot synthesis is advantageous due to the ease of operation without isolating the intermediates, and it is also more time efficient and often higher yielding. However, the most popular "click" reactions (such as CuAAC, SPAAC, and TECC) are not completely orthogonal to each other,[29] so a one-pot "click" approach toward giant surfactants has not yet been demonstrated. To address this problem, we must either use other "click" reactions that are orthogonal to the above-mentioned reactions or perform these reactions in a one-pot procedure with sequential addition of the reactants.

The oxime ligation refers to the condensation reaction between an aminoxy group and an aldehyde or ketone to form an oxime linkage and has attracted considerable interest as a highly reactive, high-yielding, bio-orthogonal "click" reaction under physiological conditions.[29,39] Many reports have demonstrated the utility of oxime condensation in the synthesis of functional soft polymeric materials including polymer−protein giant amphiphiles,[40] biomacromolecular immobilization films,[41,42] and swollen cross-linked gels.[43] Taking advantage of its orthogonal nature to CuAAC/SPAAC/TECC, oxime reactions may be ideal to achieve one-pot "click" synthesis of POSS-based giant surfactants when used in combination with other established "click" reactions.

In this letter, we describe a modular and efficient one-pot approach for the preparation of POSS-based giant surfactants by using different orthogonal "click" chemistries under mild conditions (Scheme 1). The method is demonstrated in two model systems: single-tailed giant surfactant and asymmetric, multitailed giant surfactant.

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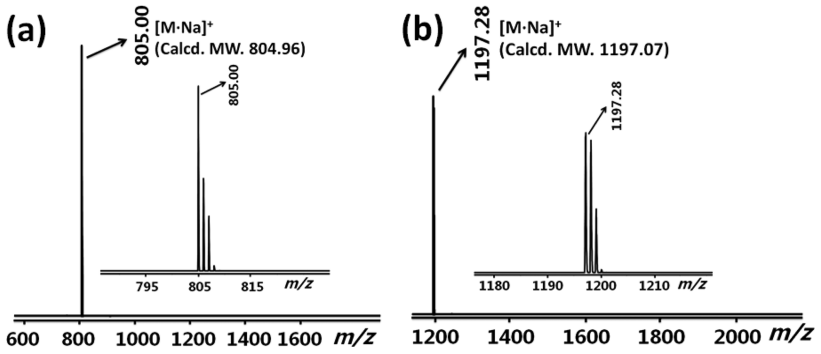

Figure 1. MALDI-TOF mass spectra of (a) VPOSS-CHO and (b) CHO-(VPOSS)-DIBO. The zoom-in view provided in the inset shows the isotope pattern of the $[M{\cdot}Na]^+$ ion for each sample.

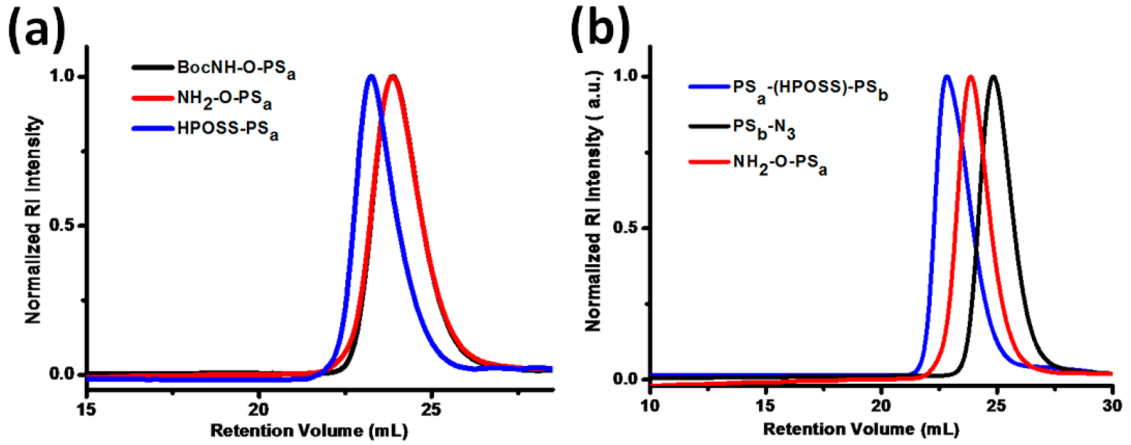

Figure 2. SEC overlays for polymers: (a) BocNH-O-PS_a (black curve), NH_2-O-PS_a (red curve), and HPOSS-PS_a (blue curve) and (b) PS_b-N_3 (black curve), NH_2-O-PS_a (red curve), and PS_a-(HPOSS)-PS_b (blue curve).

The installation of "click" functionalities onto a POSS cage is an important step to prepare POSS-based "clickable" precursors for giant surfactants. Although "click" reactions have been widely applied in the design and synthesis of giant molecules, the potential of performing several "click" reactions either simultaneously or sequentially in a one-pot procedure remains largely unexplored. While "click" reactions are supposed to be ideally orthogonal to each other, the extent of their mutual orthogonality varies in reality.[29] For example, the alkyne groups that can undergo CuAAC reaction (terminal alkynes) or SPAAC reaction (strained alkynes) are also susceptible to thiol-yne reaction.[44,45] Therefore, the number of pairs of the ideally orthogonal "click" reactions is quite limited. To design a one-pot synthetic route that is applicable under a broad range of conditions without any interference, it is critical to develop POSS-based precursors with functional groups that are of orthogonal reactivities.

We specifically designed two types of "clickable" building blocks, VPOSS-CHO and CHO-(VPOSS)-DIBO, for the facile one-pot synthesis of POSS-based giant surfactants under mild conditions. The former contains two kinds of "click" functionalities, a vinyl group for TECC and an aldehyde group for oxime ligation, while the latter possesses a vinyl group, aldehyde group, and 4-dibenzocyclooctyne (DIBO) motif for TECC, oxime ligation, and SPAAC "click" reactions, respectively. The synthetic procedures are quite similar to the established methods for VPOSS-alkyne[28] and alkyne-(VPOSS)-DIBO[18] reported in our pervious work. For example, VPOSS-CHO can be prepared by the esterification of a monohydroxyl-functionalized heptavinyl POSS (VPOSS-OH) with 4-formylbenzoic acid in a very good yield (>90%) (Scheme 1A). Similarly, CHO-(VPOSS)-DIBO is designed and synthesized by the sequential esterification of the precursor HO-(VPOSS)-OH first with equimolar amounts of 4-formylbenzoic acid on the primary hydroxyl group and then with the DIBO-COOH on the secondary hydroxyl group in the presence of DPTS and DIPC in excellent yields (Scheme 1B). Notably, the first esterification occurs selectively in primary alcohol.[14,17]

Both of those two POSS-based "clickable" precursors are thoroughly characterized by ^{1}H NMR, ^{13}C NMR, and MALDI-TOF mass spectrometry to confirm their identity and uniformity. The most convincing evidence is provided by the MALDI-TOF mass spectra (Figure 1) where only one peak matching the mass of the proposed structures is observed. The observed peaks at m/z 805.00 in Figure 1a and at m/z 1197.28 in Figure 1b agree perfectly with the calculated monoisotopic molecular mass for VPOSS-CHO ($C_{24}H_{30}NaO_{15}Si_8$ 804.96 Da) and CHO-(VPOSS)-DIBO ($C_{47}H_{50}NaO_{19}SSi_8$ 1197.07 Da). Moreover, the successful introduction of the formylbenzoic group in VPOSS-CHO is evident by the appearance of new peaks at δ 10.09 which corresponds to the formyl group and δ 8.18 and 7.93 ppm which correspond to the aromatic protons in the ^{1}H NMR spectrum (Figure S1a, Supporting Information). Similarly, the complete reaction of CHO-(VPOSS)-DIBO is confirmed by the disappearance of the resonances at δ (4.52−4.37) and 4.10 ppm (see ^{1}H NMR spectrum of CHO-(VPOSS)-OH in Figure S2a, Supporting Information) and the appearance of the new resonances at δ

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Table 1. Summary of Molecular Weight Characterization

sample	molecular formula[a]	m/z (calcd)[b]	m/z (obsd)[c]	$M_{n,NMR}$ (g/mol)	$M_{n,SEC}$ (g/mol)	PDI
NH_2-O-PS_a	$[C_{208}H_{213}AgNO_5]^+$	2911.55	2911.90	3.6 k	3.8 k	1.05
HPOSS-PS_a	$[C_{254}H_{291}NNa_2O_{26}S_7Si_8]^{2+}$	2132.38	2132.40	4.9 k	5.2 k	1.08
PS_a-(HPOSS)-PS_b	$[C_{427}H_{466}N_4Na_2O_{32}S_8Si_8]^{2+}$	3343.54	3343.52	7.8 k	7.3 k	1.07

[a]The molecular formula adjusted based on the observed molecular species in MALDI-TOF or ESI mass spectrometry with corresponding cations. [b]The calculated monoisotopic molecular weight. [c]Experimentally observed m/z of 25-mer of NH_2-O-PS_a with a silver ion $(M{\cdot}Ag)^+$ by MALDI-TOF, 26-mer of HPOSS-PS_a with two sodium ions $(M{\cdot}2Na)^{2+}$ by ESI, and 44-mer of PS_a-(HPOSS)-PS_b with two sodium ions $(M{\cdot}2Na)^{2+}$ by ESI.

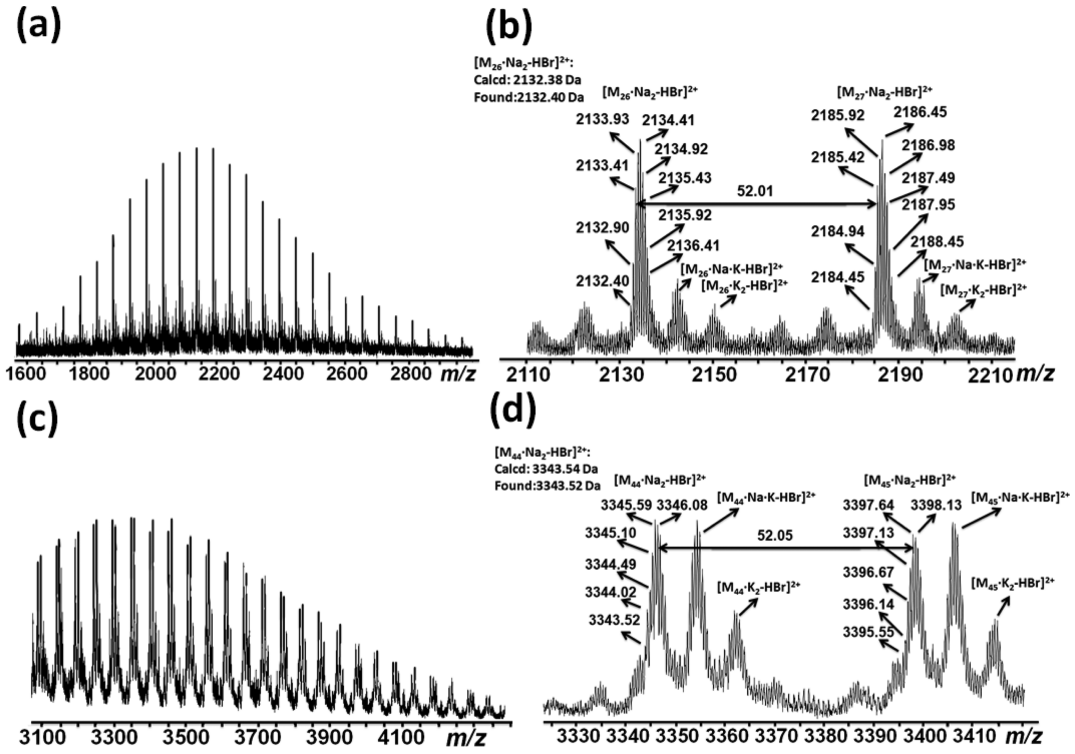

Figure 3. ESI mass spectra of HPOSS-PS_a (a, b) and PS_a-(HPOSS)-PS_b (c, d), among which panels a and c are overviews of the spectra and panels b and d are the magnified views of the spectra within a specific mass range to illustrate the mass differences between two adjacent peaks and their monoisotopic patterns.

5.38, 4.64, and 4.44 ppm in the ^{1}H NMR spectrum of the product in Figure S3a (Supporting Information). Specifically, the successful attachment of the DIBO motif is demonstrated by the observation of characteristic proton resonances at δ 5.58, 3.18, and 2.95 ppm in the ^{1}H NMR spectrum of CHO-(VPOSS)-DIBO (Figure S3a, Supporting Information).[18] Therefore, all the characterization results unambiguously confirm the molecular structures and uniformity of the two "clickable" building blocks, which may serve as versatile precursors for the facile one-pot synthesis of POSS-based giant surfactants.

The newly designed "clickable" precursor, VPOSS-CHO, is employed for the simultaneous one-pot synthesis of a single-tailed giant surfactant. The success of this synthetic route highly relies on the orthogonal nature of oxime ligation and TECC. The amino-oxy chain-end functionalized hydrophobic polymer (NH_2-O-PS_a) was prepared according to the established method reported by Maynard et al. (Scheme S1, Supporting Information)[40] and fully characterized utilizing ^{1}H NMR (Figure S4a, Supporting Information), ^{13}C NMR (Figure S4b, Supporting Information), SEC (Figure 2), and MALDI-TOF mass spectrometry (Figure S5, Supporting Information, and Table 1) to establish its identity and the uniformity of the molecular structure. The simultaneous one-pot "click" synthetic process is simply performed by mixing the "clickable" precursor VPOSS-CHO (1.0 equiv), the polymer tail NH_2-O-PS_a ($M_{n,NMR}$ = 3.6 kg/mol, PDI = 1.05, 1.0 equiv), the functional thiol 2-mercaptoethanol (10.0 equiv) in a common solvent (such as $CHCl_3$ or THF) that contains *p*-toluenesulfonic acid (TsOH) as the catalyst for oxime ligation (5 mg), and 2,2-dimethoxy-2-phenylacetophenone (DMPA) as the photoinitiator for TECC (2 mg). The mixture is then irradiated with UV 365 nm for 30 min to completely finish the reaction. The purification does not need a chromatographic process, and all the byproducts can be easily removed by repeated precipitation into cold methanol.

The success of the one-pot reaction is fully supported by the evidence from NMR, FT-IR, SEC, and electrospray ionization (ESI) mass spectrometry. The complete thiol−ene functionalization of the VPOSS head is revealed by the disappearance of the vinyl protons in the resonance range of δ (6.16−5.84) ppm in the ^{1}H NMR spectrum (Figure S1b, Supporting Information) and sp^2 carbon resonances at δ 137.08 and 128.52 ppm (Figure S6, Supporting Information) in the ^{13}C NMR spectrum of the resulting giant surfactant. This result is also in accordance with the new resonances emerging in the

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range of δ 3.87 and 2.86 ppm in the ^{1}H NMR spectra, which are attributed to the characteristic protons of the newly formed thiol−ether bonds. On the other hand, the resonance at δ 10.09 ppm which is attributed to aldehyde proton (b) in VPOSS-CHO (Figure S1a, Supporting Information) completely disappears in the ^{1}H NMR spectrum of hydroxyl-functionalized POSS (HPOSS)-PS$_a$ (Figure S1b, Supporting Information), suggesting the close to quantitative conversion of the aldehyde group. Moreover, it is also evident that VPOSS-CHO displays two resonances at δ −68.0 (−*Si*CH$_2$CH$_2$−) and δ −80.0 (−*Si*CH═CH$_2$), while HPOSS-PS$_a$ only exhibits a single resonance at δ −68.0 (−*Si*CH$_2$CH$_2$−) in the ^{29}Si NMR spectra (Figure S7, Supporting Information),[17,19] indicating the successful thiol−ene multiple addition reaction. In addition, the FT-IR spectra (Figure S8, Supporting Information) can also provide the direct evidence for the success of the one-pot reaction. Compared with the spectrum of NH$_2$−O−PS$_a$, the new strong absorbance bands at around 3300 cm^{-1} are observed in the spectrum of the final product (Figure S8, Supporting Information), revealing the success of TECC reaction. The SEC trace of HPOSS-PS$_a$ (M_n = 5.2 kg/mol, PDI = 1.08) (Table 1) (Figure 2a) shows single symmetric distribution which shifts to a lower retention volume relative to that of NH$_2$−O−PS$_a$ due to an increase of molecular mass. Furthermore, the ESI mass spectrum in Figure 3a shows only one single narrow distribution with molecular weights in accordance to the proposed structure. A representative monoisotopic mass peak at m/z 2132.40 for HPOSS-PS$_a$ (two Na$^+$ adduct) is in perfect agreement with the calculated molecular mass of 2132.38 Da for 26-mer of $[C_{254}H_{291}NNa_2O_{26}S_7Si_8]^{2+}$ (Figure 3b and Table 1). The isotope spacing ($\Delta m/z$) in their isotopic patterns is 0.5 amu, indicating the species are in their doubly charged states (Figure 3b). Therefore, it can be concluded that the model single-tailed giant surfactant, HPOSS-PS$_a$, is synthesized by single-step one-pot process with simultaneous oxime ligation and TECC reactions.

Notably, the one-pot synthetic strategy for giant surfactants holds many promising features from both "click" reactions, such as minimum setup, short reaction time, easily scalable, mild experimental conditions, and nonchromatographic purification. Even compared with the sequential "click" approach that we reported previously,[17,28] it is still advantageous in that (1) it only takes 30 min to prepare a precisely defined giant surfactant, while the former usually takes one day; (2) it features a metal-free process and may be easily adapted to incorporate biopolymers/bioligands into the system to further expand the scope of giant surfactants;[39,40] and (3) the reaction is conducted under mild conditions in the presence of oxygen and moisture. Above all, the facile one-pot "click" synthetic strategy seems to be a general, robust, and simple method to generate a library of giant surfactants possessing one functional POSS head tethered with one polymer tail.

It has been known that the self-assembly behavior of giant surfactants is found to be very sensitive to their primary chemical structures such as topological variation. For example, a pair of topological isomers that possess identical volume fraction of PS tails but distinct polymer topologies (such as dihydroxyl-functionalized POSS (DPOSS)-PS$_{35}$ and DPOSS-2PS$_{17}$, i.e., one head-one tail vs one head-two tails) was found to show distinct self-assembly behaviors. The former self-organizes into a double gyroid structure in the bulk, while the latter generates a hexagonally packed cylinder structure.[8] A similarly exceptional sensitivity has also been observed in solution: carboxylic acid-functionalized [60]fullerene (AC$_{60}$)-PS$_{44}$ forms spherical micelles, while AC$_{60}$-2PS$_{23}$ forms bilayer vesicles under the identical conditions.[9] Considering that XPOSS-PS$_{2n}$ and XPOSS-2PS$_n$ represent the most typical cases of the topological isomeric giant surfactants, it is highly desirable if a series of topological isomers based on one POSS head tethered with two PS tails of different tail lengths can be synthesized facilely. In this way, a quantitative investigation of the topological effects may be conducted using this library of compounds.

While this type of asymmetric, multitailed giant surfactant can be synthesized by our recently reported sequential triple "click" approach, the former method cannot be easily adapted to a one-pot process.[18] Multistep synthesis and extensive purifications are usually required. Herein, the oxime ligation, SPAAC, and TECC are combined to achieve one-pot synthesis of an asymmetric, multitailed giant surfactant composed of one hydrophilic POSS head tethered with two PS tails of different lengths. A POSS-based building block containing three different "click" functionalities, CHO-(VPOSS)-DIBO, is employed as a versatile precursor. Notably, this precursor possesses three distinct "clickable" functionalities for oxime ligation, SPAAC, and TECC, respectively. While oxime ligation is truly orthogonal to both SPAAC and TECC, the latter two may interfere with each other if performed simultaneously due to the potential thiol-yne reaction.[44,45] Therefore, a sequential multistep procedure, rather than simultaneous single-step reaction, is employed to achieve the one-pot synthesis.

The synthesis is conveniently conducted by mixing equimolar amounts of CHO-(VPOSS)-DIBO with NH$_2$-O-PS$_a$ (the long tail, $M_{n,NMR}$ = 3.6 kg/mol, PDI = 1.05) and azido-functionalized PS (PS$_b$-N$_3$, the short tail, M_n = 2.6 kg/mol, PDI = 1.04) in a common solvent. After the addition of a few milligrams of TsOH as the oxime ligation catalyst, the mixture is stirred at room temperature for 1.75 h. Without any further purification, the thiol ligand and photoinitiator are then directly put into the solution followed by another 15 min of irradiation under UV. After repeated precipitation into cold methanol, the product PS$_a$-(HPOSS)-PS$_b$ was obtained as a white powder in a good yield (∼85%).

Similar to HPOSS-PS$_a$, the success of the thiol−ene modification of the VPOSS cage is supported by the NMR spectra. The ^{1}H NMR resonances in the range of δ (6.16−5.86) ppm, corresponding to the vinyl group, completely disappeared in the resulting product, and the new protons at the thiol−ether linkages can be clearly found at around δ 3.79 and 2.76 ppm (Figure S3b, Supporting Information) as discussed before.[14] The sp^2 carbon signals for the vinyl group at δ 137.38 and 128.77 ppm (Figure S9, Supporting Information) in the ^{13}C NMR spectrum are also completely missing. In addition, no peak at δ 10.08 ppm is observed in the ^{1}H NMR spectrum of PS$_a$-(HPOSS)-PS$_b$, suggesting the complete consumption of the aldehyde group during the oxime ligation reaction. Moreover, two new distinct characteristic peaks at δ 6.23 and 6.08 ppm corresponding to the proton (c) on the DIBO in the ^{1}H NMR spectrum of the product are originally shifted from the single peak at δ 5.58 ppm in the "clickable" precursor's spectrum, indicating the efficient and successful introduction of a short PS tail onto the POSS surface via SPAAC reaction (Figure S3, Supporting Information).[18,46] This is in good agreement with both of the FT-IR (Figure S10, Supporting Information) and UV−vis absorbance (Figure S11,

Supporting Information) results. After the one-pot reaction, the disappearance of the strong characteristic vibrational band for the azide group of PS_b-N_3 at ~2098 cm^{-1} (Figure S10, Supporting Information)[28] as well as the strong absorbance for the DIBO motif of CHO-(VPOSS)-DIBO at 306 nm in the UV−vis spectrum (Figure S11, Supporting Information)[18,35] reveal the complete stoichiometric SPAAC reaction between the precursor and azido-functionalized polymer. The SEC trace of PS_a-(HPOSS)-PS_b (Figure 2b) shows a monomodal, symmetric peak with a narrow molecular mass distribution (M_n = 7.3 kg/mol, PDI = 1.07). There is a clear shift in retention volume compared to NH_2-O-PS_a (M_n = 3.8 kg/mol, PDI = 1.05) or PS_b-N_3 (M_n = 2.6 kg/mol, PDI = 1.04), revealing the increased molecular mass. Furthermore, the structural homogeneity and purity of the targeted product are also validated by ESI mass spectrometry (Figure 3c and 3d). The overview of the spectrum exhibits one main distribution with molecular masses in accordance with the proposed structure (e.g., for 44-mer with the formula of $[C_{427}H_{466}N_4Na_2O_{32}S_8Si_8]^{2+}$, observed m/z 3343.52 Da vs calcd 3343.54 Da) (see Table 1). These results unambiguously confirm the molecular structure and uniformity of the product. This sequential multistep one-pot strategy is thus able to provide a general and straightforward methodology to synthesize a family of topological isomers based on asymmetric multitailed giant surfactants. This methodology should be easily extended to the facile one-pot synthesis of many other types of giant molecules with even more complex macromolecular architectures, such as POSS-based multiheaded and multitailed giant surfactants.[18] Most importantly, using this methodology, each block in these giant surfactants can be precisely controlled and systematically varied.

In summary, we have successfully developed a one-pot "click" strategy based on a series of orthogonal "click" reactions and used this strategy to generate two types of model giant surfactants. We have shown that the strategy is a general, robust, and efficient methodology. Several parameters in the giant surfactants including chemical composition, molecular mass, surface functionalities of the nanoparticle, and polydispersity can be systematically varied during the reaction. This methodology can be used to generate a library of POSS-based giant surfactants for systematic investigation of their self-assembly behavior and hierarchical structure formation in the bulk, thin film, and solution states. The mild experimental conditions and metal-free orthogonal "click" methods provide numerous opportunities to construct novel, biomolecule-based giant surfactants. In addition, the pH sensitivity of the formed oxime ether linkages may also offer a promising approach to develop the first generation of stimuli-responsive giant surfactants and lipids and perhaps triggered deconstruction and release strategies.[43]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information on the synthesis and characterization of the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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